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OFFICE OF NAVAL RESEARCH
WASHINGTON, D. C.

2 January 1953
Report No. 668
(Quarterly)
Copy No. ...

INVESTIGATION OF LIQUID ROCKET PROPELLANTS



Contract N7onr-462

Task Order No. III

Project No. NR 220 023

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2 January 1953

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Report No. 668
(Quarterly)

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INVESTIGATION OF LIQUID ROCKET PROPELLANTS

Contract N7onr-462

Task Order III

Project NR 220 023

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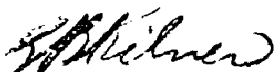
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AEROJET ENGINEERING CORPORATION

Azusa, California

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CONTRACT FULFILLMENT STATEMENT

This is the thirty-first in a series of progress reports submitted in partial fulfillment of Contract N7onr-462, Task Order III, covering the work performed during the period from 1 September through 30 November 1952. The previous reports in this series have been issued at bimonthly intervals, this being the first to cover a quarterly period.

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I. INTRODUCTION

A. In February 1948, Contract N7onr-462, Task Order III, was established for the purpose of conducting a comprehensive investigation of liquid propellants suitable for use in rocket motors. Although emphasis has generally been placed on propellant systems possessing high specific impulses, it has often been found desirable to extend the scope of this study to include the short-term investigation of problems arising with any fuel or oxidizer. Pilot plants have been designed and constructed for the manufacture of propellants not commercially available, and these materials have, in turn, been evaluated in a small rocket motor.

B. Results of the investigations have been reported in a series of bimonthly reports, an annual summary being issued at the end of each calendar year. Reports will be issued at quarterly intervals beginning with this report, and no annual summary reports will be prepared henceforth.

C. Of continuing interest to this contract is the development of a high-energy fuel possessing a freezing point below -65°F and without excessive vapor pressure at ambient temperatures. Thus, during the period covered by this report, investigations were made on the synthesis of a new compound, N-amino-ethylenimine, and a study of hydrazine additives was continued. Because of the need for an oxidizer capable of being stored in sealed tanks, research is being conducted on improving the physical properties of dinitrogen tetroxide; work has thus far been restricted to determining the effect of several functional groups on the degree of deviation from ideal freezing-point depression. Monopropellant studies on this contract consist of investigations into the kinetics of decomposition of nitromethane at high pressures. A mass spectrometer and a polarograph are used to determine the extent and manner of decomposition of nitromethane samples placed in a furnace at various initial pressures. Motor testing during this period consisted of a short performance evaluation of "HF-D" hydrocarbon mixture with liquid oxygen, and preliminary work on the determination of the ignition delay of triethyl trithiophosphite with specially prepared WFNA at three different temperatures.

II. KINETIC STUDY OF THE THERMAL DECOMPOSITION OF NITROMETHANE

A. INTRODUCTION

In view of the importance of nitromethane as a monopropellant, an investigation is being made into the mechanism of its thermal decomposition. Several earlier investigations of this problem have been made at subatmospheric pressures; however, this program is being carried out at nitromethane pressures up to 365 psia, in an attempt to simulate more closely the conditions in a rocket combustion chamber. In the earlier work, the progress of the reaction was followed by observation of the variation of total pressure with time. In the present program, it has been possible to determine directly the amount of nitromethane remaining in the partially reacted samples. This procedure allows

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interpretation of the results to be independent of any postulates concerning the number of moles of product resulting from the decomposition of each mole of nitromethane; thus it allows direct determination of the order of the decomposition with respect to nitromethane concentration. Identification and determination of the relative amounts of products of the decomposition by mass-spectrometer analysis will give more direct evidence for the actual mechanism. During this report period, the main objectives have been to ascertain the order of the reaction with respect to nitromethane at a temperature of 355°C and at pressures up to 365 psia, and to determine the principal intermediate and final decomposition products.

B. ORDER OF THE REACTION

1. Frequently, in kinetic studies of complex reactions, the concentration of the reacting compound is determined intermittently or continuously during the course of each experiment. In this way, the rate of the reaction at zero time can be obtained by extrapolation, for each set of initial conditions. In this work, because of difficulties imposed by the high pressures, the alternative was chosen of studying the amount of decomposition in a constant time interval as a function of initial pressure. This technique allows the use of small samples of nitromethane, sealed into glass ampoules, inasmuch as each sample point is the result of a separate experiment.

2. Weighed amounts of nitromethane were sealed into Pyrex ampoules of 2 to 3 ml volume, immersed in a salt-bath at a controlled temperature for constant times, and quenched rapidly to room temperature. The ampoules were then broken, and the contents analyzed for remaining nitromethane. The initial pressure was calculated from the loading density of the ampoules, assuming that the perfect gas law holds at the temperatures involved. Residual nitromethane was analyzed by means of a polarograph as described in Reference 1. After separation of the nitromethane from the more volatile reaction products, it was diluted quantitatively with 0.05M sulfuric acid and the polarogram of the resulting solution was determined. A representative polarographic wave for nitromethane is shown in Figure 1; the height of the diffusion current wave thus obtained is, in the concentration range used for analysis, proportional to the concentration of nitromethane. Figure 2 is the calibration curve for the analyses, prepared from the analyses of samples containing known amounts of nitromethane.

3. For constant temperature and reaction time, the integrated rate equations for order 1, 3/2, and 2 with respect to nitromethane reduce to the following:

First order: $\log_e \frac{C}{C_0} = K_1$

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Three-halves order:
$$\frac{1}{C^{\frac{1}{2}}} - \frac{1}{C_0^{\frac{1}{2}}} = K_{3/2}$$

Second order:
$$\frac{1}{C} - \frac{1}{C_0} = K_2$$

where

C_0 , C = initial and final concentrations of nitromethane
 K_1 , $K_{3/2}$, K_2 = constants, proportional to the rate constants

Each of these expressions is formally independent of concentration or pressure. By calculating the values of the functions at experimental points over a range of pressures, the approximate order of the reaction can be determined.

4. A series of thermal decomposition tests was performed at 355°C for a period of 31 min and at varying initial pressures. Figure 3 gives the percent decomposition ($100 \times (1 - C/C_0)$) of nitromethane as a function of calculated initial pressure. It is seen, despite the rather large scatter in the data, that there is a definite dependence of percent decomposition upon initial pressure. The dependence cannot be the result of the assumption that the nitromethane behaves as a perfect gas, because the calculated percent decomposition is independent of this assumption. Table I shows the calculated values of the functions defined above, each normalized to a mean of 100 to better show the trends. If the reaction were truly first-order, the values of K_1 of the table (as well as the points of Figure 3) would show no dependence on pressure. Below approximately 300 psia, the apparent order of the reaction is between 1 and 3/2, whereas above 300 psia, indications are that the order is approaching 2. Previous investigators (Reference 2) have found evidence for a first-order law at subatmospheric pressures. Their data, extrapolated to the lower temperature of this work, would indicate approximately 18% decomposition at a pressure of 6 psia, which is not inconsistent with the results shown in Figure 3. Because of this deviation from the first-order decomposition found at low pressures, additional tests will be run to confirm the apparent second-order character of the reaction at high pressures.

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5. The reaction appears to be mainly homogeneous, as shown by experiments with ampoules to which Pyrex rods had been added. A four-fold increase in the surface-to-volume ratio produced only a 9% increase in decomposition. In another case, a $3\frac{1}{2}$ -fold increase in the surface to volume ratio produced a 4% increase in decomposition. The contribution of the Pyrex walls should therefore not be more than 2 to 3%, which is within the experimental error.

C. PRODUCTS OF THE REACTION

1. A General Electric mass spectrometer was used in identifying the principal intermediate and final reaction products.

2. Two samples were decomposed only partially in order to identify any intermediate reaction products which might also be final products. The only compound identified thus far as a reaction intermediate which does not appear as a final product is nitric oxide. All other compounds appearing in the partly decomposed samples also appear as final products.

3. The following materials are the principal final decomposition products of nitromethane under the conditions of high pressure employed in these tests: carbon dioxide, carbon monoxide, water, nitrous oxide, nitrogen, hydrogen cyanide, acetonitrile, and methane. A few other materials are present in trace amounts, but they have not yet been identified. The average concentrations of the principal products are given in Table II. Additional tests are being made to confirm the values.

4. A comparison of the partially decomposed and totally decomposed samples, as given in Table II, indicates the following trends:

a. The relative amounts of carbon dioxide and acetonitrile remain approximately constant as the decomposition proceeds.

b. Nitrous oxide and methane appear as final decomposition products, but do not appear as intermediates. It is possible, however, that their concentration in the partially decomposed samples was below the limits of detection under the experimental conditions employed.

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of Nitromethane, C (cont.)

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c. The concentration of hydrogen cyanide appears to be greater in the partially decomposed samples than in the completely decomposed ones. This may either result from the reaction of hydrogen cyanide with some reaction intermediates, or from its thermal decomposition.

d. The concentration of nitrogen and carbon monoxide is greater in the totally decomposed samples than in the partially decomposed ones.

5. Two ampoules containing only acetonitrile were heated in the furnace for a length of time sufficient for the complete decomposition of nitromethane. The mass spectrometric analyses indicated that acetonitrile decomposed less than 5% under the experimental conditions employed, so that, because of the small amount of acetonitrile in the decomposed nitromethane samples, the contribution of decomposition products of acetonitrile may be neglected in the consideration of the nitromethane decomposition.

6. Table III lists the decomposition products found by Cottrell, Graham, and Reid (Reference 2) for the reaction at 230 to 400 mm initial pressure, and at temperatures ranging from 380 to 410°C. Only materials which were volatile at -78°C were included by the authors. For comparison, the results of the Aerojet work for approximately the same extent of decomposition have been recalculated to exclude water and are also listed in Table III. The differences between the two sets of data are discussed below.

a. Acetonitrile and hydrogen cyanide have vapor pressures of less than 1 mm at -78°C, so that it is not surprising that Cottrell et al. did not detect these components in the gas phase of their product. Even though they did not find these materials in measurable amounts in the liquid phase, they occasionally detected the faint odor of hydrocyanic acid in their products. The concentrations of hydrogen cyanide and acetonitrile would be expected to be higher in this research. They are probably formed by a bimolecular process, which would be favored by higher pressures.

b. Nitric oxide was considered by Cottrell et al. to be the primary nitrogen-containing compound; they find that it decreases from about 60 mole% to 45 mole% as the decomposition reaches about 40%. In this work it was found that nitric oxide comprised about 20 mole% of the decomposition products in the partially decomposed samples and was absent in the completely decomposed ones, so that qualitatively at least the results of the two investigations are similar in this respect. In this laboratory it has been found, however, that more than half of the available nitrogen is in the

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form of nitrogen molecules in the partially decomposed samples, and that the increase in nitrogen gas in the completely decomposed samples corresponds to the decrease in nitric oxide. In this sense the results are consistent on an atom-balance basis.

c. Cottrell and co-workers found more carbon monoxide and less carbon dioxide than is found in this work. There is as yet insufficient information to explain this difference, although again some qualitative agreement is obtained. In both cases the carbon dioxide concentration remains virtually constant, and the carbon monoxide concentration increases as the decomposition proceeds.

d. More data are needed to explain the large difference in the methane concentration in the two investigations.

III. IMPROVEMENT OF DINITROGEN TETROXIDE AS A ROCKET OXIDIZER

A. INTRODUCTION

Because of its relatively high freezing point (-11.2°C), dinitrogen tetroxide has not received serious consideration as a rocket oxidizer for Service use. In recent years the so-called "mixed oxides" (dinitrogen tetroxide and nitric oxide) have become commercially available, and although this mixture has a freezing point low enough to prevent solidification under any normal field conditions, the vapor pressure becomes excessive at even moderately high temperatures. In an attempt to render dinitrogen tetroxide more valuable for wide-scale rocket application, a search is being conducted for additives that will lower its freezing point without increasing the vapor pressure. By noting the effect of a variety of functional groups on the degree of deviation from ideality, it is hoped that it will be possible to select one or more successful additives that will be superior to any selected by mere random trial of many compounds. Stability and corrosivity of any selected solutions will be studied before final recommendations are made.

B. APPARATUS

Apparatus normally used for the measurement of low-temperature freezing points depends on some relatively gentle oscillatory motion of the cooling liquid for the establishment of equilibrium. Such stirring tends to fail exactly when it is most needed, that is, at the first appearance of solids, and generally after some degree of supercooling. It is difficult to construct an apparatus incorporating a magnetic stirrer such as is often used in titrations or reactions requiring an inert atmosphere, because such stirrers are driven from below, and in the case of a freezing-point apparatus this area is obstructed by insulating jackets and the cooling bath. As a torus of Alnico metal of a convenient size, together with apparatus for magnetizing it were available to this contract, it was possible to construct

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III Improvement of Dinitrogen Tetroxide as a
Rocket Oxidizer, B (cont.)

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the apparatus shown in Figure 4. The stirrer shaft is driven by a cylindrical Alnico magnet, at present unprotected. It is planned to coat this magnet with Teflon, thereby rendering the entire stirrer unit corrosion-resistant to everything except HF. The major advantage of the stirrer is the absence of a rotating seal, which permits its use with air- and water-sensitive systems. Although the stirrer has on occasion been operated at speeds in excess of 1000 rpm, thorough equilibrium is noted at considerably lower speeds. The apparatus was first used to locate the eutectic of the system nitromethane and dinitrogen tetroxide. The higher-temperature portion of the curve was reported in Reference 3. It was found that the freezing temperatures observed with the original equipment were consistent with those obtained by the above-described apparatus at temperatures above -35°C . Below this point the better equilibrium obtained with the high-speed stirrer shifts the former curve toward somewhat higher temperatures. The complete corrected curve is shown as Figure 5.

C. EXPERIMENTAL EVALUATION OF FREEZING POINT ADDITIVES

1. Reference 3 presented the freezing-point diagrams for several alkoxy compounds in dinitrogen tetroxide. These compounds are interesting not primarily for direct application as freezing-point depressants for dinitrogen tetroxide, but because of their rather large negative deviation from ideality. It is hoped that by studying a sufficient number of such series, it will be possible to select a compound for actual service use that might not have been obvious beforehand. In addition, the conclusions drawn from this study will perhaps make it possible to synthesize a compound with the desired properties, if one is not immediately available.

2. Three additional alkoxy compounds were investigated during this report period. The compounds were diethyl carbonate, $\text{C}_2\text{H}_5\text{O}-\text{C}(=\text{O})-\text{OC}_2\text{H}_5$; diethyl oxalate, $\text{C}_2\text{H}_5\text{O}-\text{C}(=\text{O})-\text{C}(=\text{O})-\text{OC}_2\text{H}_5$; and diethyl Cellosolve, $\text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2\text{OC}_2\text{H}_5$.

Freezing-point diagrams for these compounds with dinitrogen tetroxide are presented as Figures 6, 7, and 8. All exhibit negative deviation, the degree of which is indicated in Table IV.

3. Nitromethane in 30 wt% concentration reduces the freezing point of dinitrogen tetroxide to -35°C , without an adverse affect upon the ignition qualities of the oxidizer with hypergolic fuels (Reference 4). However, a concentration of 48% is necessary to reduce the freezing point to -55°C . It was hoped that the polynitromethanes would give larger negative deviations from ideality than nitromethane and allow a satisfactory reduction in freezing point with a smaller concentration of additive. However, the

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III Improvement of Dinitrogen Tetroxide as a Rocket Oxidizer, C (cont.)

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results obtained with the two compounds tested, tetranitromethane and trinitromethane, are disappointing in that both give positive deviations from ideality, and accordingly a very large weight percent of additive would be necessary to depress the freezing point to even minimum requirements. The diagrams for these systems are shown in Figures 9 and 10.

4. In order not to overlook any possibility of being able to depress the freezing point of dinitrogen tetroxide by the addition of a common oxidizer, the use of concentrated hydrogen peroxide was considered. A specially prepared sample of hydrogen peroxide, analysing higher than 98%, was slowly added dropwise to dinitrogen tetroxide at 0°C. As each drop touched the surface a vigorous reaction occurred, with the evolution of a considerable quantity of gas. It is not yet known whether the gassing is caused by loss of oxygen from the peroxide due to a high heat of solution, or whether peroxynitric acid (HNO_4), a possible reaction product, is decomposing under these conditions. By distilling dinitrogen tetroxide onto a cooled sample of hydrogen peroxide under vacuum, it should be possible to determine whether or not a stable mixture can be prepared. In the water and dinitrogen tetroxide system, the region of two phases extends from 18 to 87 mole% N_2O_4 at 20°C; hence, it is possible that, even if a stable solution with hydrogen peroxide can be obtained, limited miscibility might prevent a useful depression of the freezing point.

D. THERMAL STABILITY OF LOW-FREEZING DINITROGEN TETROXIDE SOLUTIONS

1. Once an additive has been selected for consideration as a freezing-point depressant for dinitrogen tetroxide on the basis of its degree of lowering and apparent stability, it will be necessary to prove conclusively that the mixture is not only safe to handle, but also that no slow reactions are occurring which might alter the original properties of the solution. The exact method used to determine this stability will depend to a large extent upon the mixture in question. A very simple test can be used, however, for establishing the relative hazard in handling various solutions in the laboratory. This qualitative test involves the sealing of a small quantity of the test solution within a sealed bomb equipped with a rupture disk, and heating the bomb until explosion occurs. The temperature of autodecomposition can then be compared with the known stability of other solutions in the same apparatus.

2. Selected solutions of some of the additives evaluated as freezing-point depressants were sealed within a small bomb and heated at the rate of 10°F/min. Results shown in Table V indicate that solutions of trioxane and diethyl Cellosolve in dinitrogen tetroxide should be handled with extreme caution and in limited quantities.

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IV Research on the Preparation of New Rocket
Propellants, B (cont.)

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consequently considered that the isolated solid was ethanolhydrazinium sulfate, $(\text{HOCH}_2\text{CH}_2\text{NH}_2\text{NH}_2)^+ (\text{HSO}_4)^-$. At 110° the solution was decidedly yellow,* and set to a glass at room temperature. Partial crystallization occurred after three days at 0°C , but the process was extremely slow, and isolation of the crystallized from the uncrystallized portion was not accomplished. Further attempts were made to crystallize the material by reducing its viscosity; several solvents (water, ethanol, methanol) were employed, but crystallization did not occur. At 160°C the solution was orange, and set to a glass which did not crystallize after two weeks at 0°C . Further heating resulted in a violent exothermic reaction at about 170°C . The temperature suddenly rose to 260°C , and the mass blackened and became cokelike in appearance. That oxidation (probably of the hydrazine function) rather than charring occurred is indicated by the fact that the reaction products were water-soluble, and the odor of sulfur dioxide was easily discernible.

c. The removal of the elements of sulfuric acid from the ester was attempted by a flash distillation of the ester with hot aqueous sodium hydroxide, according to the directions of Reeves (References 6 and 7). The ester was dissolved in the calculated amount of cold 14% sodium hydroxide, and added dropwise to a well-stirred 14% solution of boiling sodium hydroxide. The distillate was collected at -5°C , and the product salted out by addition of solid sodium hydroxide. The 160° portion (orange glass) gave about 10% of the expected amount of oil.** The 110° portion (yellow glass, partially crystalline) gave, on this occasion, about 85%. However, in subsequent experiments it was not found possible to reproduce these results; in six experiments the best yield was only about 10%. The crude oil was alternately dried over sodium hydroxide and fractionally distilled from solid sodium hydroxide. The product obtained had a boiling range of $54-8^\circ\text{C}$ at 102 mm.

d. Variations of this method for the dehydration of ethanolhydrazine were tried in an attempt to increase the yield of product.

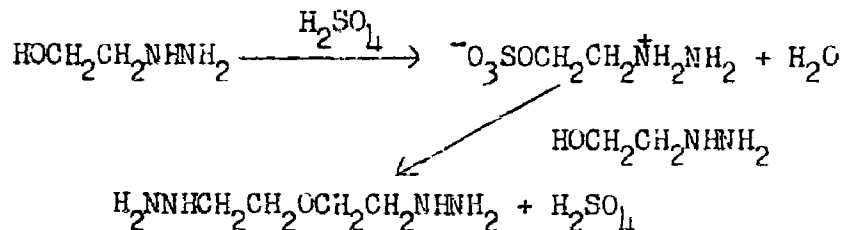
(1) When the ethanolhydrazine and sulfuric acid mixture was heated rapidly over a free flame to 110° , and the mixture maintained for 30 min at this temperature, only 70% of the reaction water was recovered, but the resulting yellow glass gave a 35% yield of crude product in the subsequent flash distillation. This suggests that the formation of an ether at lower temperatures reduced the yield of desired product in the experiments wherein slow heating was employed:

* A dry-ice trap placed between the system and pump had collected 82% of the calculated water of reaction by the time this temperature had been reached.
** The yield reported here is based on the weight of crude (wet) product.

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(2) Further experiments with the ethanolhydrazine and sulfuric acid mixture, in which the time of reaction, temperature, and mode of addition* were varied produced no increase in the yield of product.

(3) Variations in the conditions employed in the subsequent flash distillation of the ester produced little or no change in the yield of desired product. The variables considered were the amount and concentration of sodium hydroxide in the boiler, the amount of sodium hydroxide used in salting out the product, and the temperature employed in salting out. If a mixture of the ester and the calculated amount of a 14% sodium hydroxide solution were simply heated without employing a flash distillation, no product was obtained from the aqueous distillate.

2. In order to avoid undesirable oxidation at high temperatures, phosphoric acid was substituted for sulfuric acid as the esterifying agent (Reference 8). At 160 to 180°C the reaction mixture became dark brown and completely opaque. At 130°C a yellow glass was obtained; a flash distillation of this material afforded no product. A similar experiment with ethanolamine at 160 to 180°C failed to give a crystalline ester. Apparently this reaction represents a true catalytic dehydration without intermediate ester formation. Inasmuch as ethylenimine is known to polymerize readily under acidic conditions, it is presumed that any N-aminoethylenimine formed would polymerize readily in the acidic medium employed.

3. An attempt was made to prepare N-aminoethylenimine by the dehydrohalogenation of 2-bromoethylhydrazine. The method has been described by Gabriel (References 9 and 10). A chloroform solution of phosphorus tribromide was added dropwise at 0°C to a well-stirred chloroform solution of ethanolhydrazine (Reference 11). A yellow-white precipitate formed during the addition. The mixture was heated at 80°C for one hour to remove volatile materials, and the residue treated with ice water. The solution was filtered to remove a small amount of insoluble material, and the filtrate made basic with sodium hydroxide. The solution was then flash-distilled as described above, but no product could be salted out of the distillate.

*An example is the dropwise addition of ethanolhydrazine to hot (135°C) sulfuric acid. A stream of nitrogen in this experiment permitted a relatively high reaction temperature without noticeable oxidation.

4. Yields of 50% can now be obtained by a simple modification of the original esterification method. In this new technique, cold undiluted ethanolhydrazine is slowly added to excess concentrated sulfuric acid maintained at 120°C. On cooling and slowly adding small portions of ether, a crystalline product may be obtained. The sulfuric acid solution of the ester is then added to the boiling sodium hydroxide solution, while at the same time additional sodium hydroxide solution is added from another dropping funnel. The product is salted out of the distillate as before.

5. The catalytic dehydration of ethanolhydrazine over activated alumina was considered to be a possible simple and inexpensive method for the production of N-aminoethylenimine. An apparatus was constructed whereby ethanolhydrazine vapors passed through a heated tube containing activated alumina and the products of reaction were collected at -80°C. Reduced pressure promoted rapid passage of the vapor, and a stream of nitrogen was effective both as a carrier and a diluent. The conditions of rapid passage and low concentration of vapor are favorable to the isolation of low-molecular-weight materials, which are thereby removed before further reaction (such as polymerization) can occur. Furnace temperatures ranged from 300 to 500°C, and the reaction times varied according to the rate of nitrogen flow. Experiments of this nature are still in progress, and conclusive results have not yet been obtained. However, in one experiment, in which the furnace temperature was 420°C, a product was obtained having the same boiling range as that from the ethanolhydrazine and sulfuric acid experiments. The following compounds are also possible products in attempting to prepare N-aminoethylenimine by this method: $\text{H}_2\text{C} = \text{CHNHNH}_2$, vinyl hydrazine; $\text{CH}_3\text{CH} = \text{NNH}_2$, acetal hydrazone; and $\text{CH}_2\text{CH}_2\text{NHNH}_2$, ethylene hydrazine.

C. PROPERTIES OF N-AMINOETHYLENIMINE

1. The product of the ethanolhydrazine and sulfuric acid experiments is a colorless mobile liquid which tends to polymerize slightly on heating. Its boiling point at atmospheric pressure was found to be about 101°C.* A cooling curve displays no break in the region 25 to -150°C. At -80°C the liquid was mobile, by -90°C it had set to a glass, and in the range -130 to -150°C it was a translucent (noncrystalline) solid. The product was titrated with potassium iodate, and consumed 80% of the theoretical amount if a 4-electron change is assumed. A mass spectrogram of the material, in conjunction with spectrograms of pure ethylenimine and unsym-dimethylhydrazine, gave evidence of the presence of the ethylenimine ring, but also indicated the presence of a dimer, probably $(\text{CH}_2)_2\text{NHNHCH}_2\text{CH}_2\text{NHNH}_2$. Infrared spectra of these same materials lead to inconclusive results, probably because of impurities (such as the dimer) in the desired product. The material tends to discolor (yellow) at room temperature in air - a phenomenon common to alkyl hydrazines and probably due to oxidation.

*Some polymerization occurred at this temperature, and the boiling point is therefore uncertain.

2. Work is now in progress to determine the stability of the material, and to characterize it by the preparation of one or more suitable derivatives (as the p-dimethylaminobenzaldehyde hydrazone, for example). The heat of combustion will be determined for evaluation of the compound as a potential rocket fuel.

V. STUDY OF HYDRAZINE FREEZING POINT DEPRESSANTS

As no completely satisfactory additive, or group of additives, has yet been found for depressing the freezing point of hydrazine without altering desirable qualities of this fuel, the evaluation of new additives is of continuing interest under this contract. Because ethylenimine is now becoming commercially available, is potentially inexpensive, and should possess a specific impulse not much lower than hydrazine, the complete freezing point vs composition diagram was determined for solutions of this material in hydrazine.

1. The freezing-point diagram is shown as Figure 11. The fact that a solution freezing at -54°C (-65°F) must contain approximately 87 wt% ethylenimine rules out this compound as a practical depressant for hydrazine, although the low freezing point of pure ethylenimine makes it worthy of consideration on its own merits.

2. The ethylenimine was prepared by the method of Leighton and Reeves (References 5 and 6). It had a boiling range of 55.0 to 55.5°C (750 mm), and a freezing point of -69.0°C . The solution of ethylenimine in hydrazine darkened slightly after standing for two days.

VI. PERFORMANCE EVALUATION OF THE "HF-D" HYDROCARBON MIXTURE WITH LIQUID OXYGEN

A. INTRODUCTION

During this report period a complete mixture-ratio survey was made of the propellant combination of "HF-D" hydrocarbon mixture and liquid oxygen. A maximum specific impulse of 227 lb-sec/lb at a mixture ratio of 2.16 was obtained at a nominal chamber pressure of 300 psia in a 100-lb-thrust rocket motor. Although this fuel is of interest primarily because of its hypergolic activity with nitric acid, it was known that another contractor (Reaction Motors, Inc.) was evaluating the material with NFH_4 ; therefore a minimum program was conducted under this contract in order to determine how much greater specific impulse was realizable when liquid oxygen was used as the oxidizer.

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VI Performance Evaluation of the "HF-D" Hydrocarbon
Mixture with Liquid Oxygen (cont.)

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B. TEST INSTALLATION

The 100-lb-thrust rocket engine previously employed for the evaluation of propellants on this contract was used for the six tests found necessary to define the mixture ratio versus specific impulse curve. This engine is shown in Figure 12, and was described in References 12 and 13. The injector consisted of ten pairs of one-on-one impinging streams, and a double-coil turbulator was used approximately 2 in. downstream from the injector to ensure complete mixing.

C. PROPERTIES OF THE "HF-D" HYDROCARBON MIXTURE

The "HF-D" hydrocarbon mixture is a material produced by the Standard Oil Company of Indiana. Its important physical properties are shown below:

Carbon, wt%	89.6
Hydrogen, wt%	8.9
Heat of combustion, Btu/lb	16,200
Bromine No.	112.9
Maleic anhydride value	20.8
Freezing Point, °F	< -70°
Specific Gravity	
+70°F	0.935
+32	0.950
-40	0.990
Viscosity, cs	
+70°F	1.4895
+32	2.1923
-40	10.5373
ASTM Distillation, % distilled	
IBP	230°F 110°C
10	262 128
20	278 137
30	292 144
40	306 152
50	320 160
60	332 167
70	344 173
80	356 180
90	388 198
FBP	424 218

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VI Performance Evaluation of the "HF-D" Hydrocarbon
Mixture with Liquid Oxygen (cont.)

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D. ENGINE TEST RESULTS

1. Six tests were made over a mixture ratio range of 1.03 to 3.43. A summary of the data, with the performance parameters given both uncorrected and corrected for heat loss to the coolant, is given in Table VI. Plots of specific impulse, characteristic velocity, and thrust coefficient versus mixture ratio are shown in Figure 13.

2. The runs were characterized by luminous, relatively lengthy, exhaust jets; intermittent streaks indicated the presence of unburnt carbon. Combustion initiation, accomplished by burning gaseous hydrogen and oxygen in the chamber before the introduction of the main propellants, was smooth; but there was always some degree of afterburning on simultaneous termination of fuel and oxidizer flow. The chamber walls, turbulator, and nozzle were covered with carbon on each test.

3. It is concluded that unless "HF-D" shows exceedingly good hypergolic properties, its use as a rocket fuel is unjustified, as the performance with liquid oxygen compares unfavorably with that of JP-3 or JP-4.

VII. IGNITION DELAY STUDY OF TRIETHYL TRITHIOPHOSPHITE WITH NITRIC ACID

A. Contract Amendment No. 7 authorizes a portion of a study with the purpose of correlating ignition delays as measured by various laboratory apparatus with the delays actually observed in rocket motors. Several contractors have been furnished identical samples of triethyl trithiophosphate, n-heptane, and specially purified nitric acid, the composition of which is to be adjusted to 98.5% HNO_3 , 1.0% H_2O , and 0.5% NO_2 . Ignition delays will be measured at 75, 32, and -40°F for each of the following solutions:

<u>Triethyl trithiophosphate, Vol%</u>	<u>n-Heptane, Vol%</u>
100	0
90	10
80	20
70	30
60	40

B. As a special report will be issued early in 1953 covering the entire program, no details of the work will be presented at this time. In general, the equipment consists of a small thrust chamber equipped with a photoelectric cell and pressure pickup, both having output signals recorded on an oscillograph. By previously determining the time from activation of the propellant valves to the time of impingement of the fuel and oxidizer streams, it is possible to determine ignition delay, both by rate of increase of chamber pressure and by the occurrence of a steady light-producing reaction.

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TABLE I

THERMAL DECOMPOSITION OF NITROMETHANE ASSUMED RATE CONSTANTS

<u>P₀</u> psia	<u>percent</u> <u>decomposed</u>	<u>K₁</u> <u>(1st order)</u>	<u>K_{3/2}</u> <u>(3/2th order)</u>	<u>K₂</u> <u>(2nd order)</u>
98	22.0	76	115	167
145	24.6	87	106	123
162	27.8	100	116	129
177	25.8	92	101	107
188	30.7	112	122	128
234	26.1	93	90	83
247	31.2	115	103	98
263	24.4	86	77	67
288	28.8	104	91	77
298	29.1	106	91	75
321	30.0	109	91	73
366	33.0	123	97	74

Temperature, 355°C; time, 31 min

P₀, initial pressure of nitromethane

K₁, K_{3/2}, K₂, fractions of the percent nitromethane decomposed, proportional to the assumed rate constants

Table I

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TABLE II

DECOMPOSITION PRODUCTS OF NITROCELLULOSE

Product	Amount Present, Grams	
	<u>Partial Decomposition</u>	<u>Complete Decomposition</u>
Acetonitrile	5.2	5.4
Hydrogen Cyanide	11.6	8.0
Carbon Dioxide	22.8	22.4
Nitrogen Oxide		3.6
Methane		2.6
Nitric Oxide	13.1	"
Nitrogen	9.5	17.3
Carbon Monoxide	7.7	10.6
Water	30.0	30.0

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TABLE III

COMPARISON OF DECOMPOSITION PRODUCTS OF
NITROMETHANE (excluding water)

<u>Product</u>	<u>Amount present, mole%</u>	
	<u>Cottrell, et al.</u>	<u>Aerojet Research</u>
Acetonitrile	—	7.4
Hydrogen Cyanide	—	16.6
Carbon Dioxide	7	32
Carbon Monoxide	28	11
Nitric Oxide	46	19.5
Nitrogen	—	13.6
Methane	18	—

Table III

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TABLE IV

APPARENT SOLVATION NUMBERS OF ADDITIVES TO DINITROGEN
TETROXIDE AS DETERMINED FROM FREEZING-POINT LOWERING

<u>Additive</u>	<u>Wt%</u>	<u>Mole%</u>	<u>Freezing Point °C</u>		<u>Apparent Solvation No.</u>
			<u>Observed</u>	<u>Ideal</u>	
Nitromethane	23	30	-26.5	-24.5	0.3
	51	61*	-59.0	-44.0	0.3
Diethyl Carbonate	35	30	-39.0	-24.5	1.5
	43	37*	-54.0	-28.0	1.3
Diethyl Oxalate	38	28*	-38.0	-23.5	1.7
Diethyl Cellosolve	35	30	-29.4	-24.5	0.8
	53	47*	-58.5	-34.0	0.8
Tetranitromethane	46	30	-23.2	-24.5	(Positive Deviation)
	69	52*	-33.0	-37.5	(Positive Deviation)
Trinitromethane	33	23	-18.2	-21.0	(Positive Deviation)

*Eutectic Mixture

Table IV

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TABLE V

THERMAL STABILITY OF DINITROGEN TETROXIDE SOLUTIONS

<u>Additive</u>	<u>Wt% Additive</u>	<u>Vol Sample, ml</u>	<u>Explosion Temp, °F</u>
CH ₂ (OCH ₃) ₂ (Methylal)	12.4	1	546
		1	600
		1	548
		1	545
		1	550
	27.7	0.5	No explosion to 577
		0.75	570
		0.75	585
		1	541
		1	556
CH ₃ NO ₂ (Nitromethane)	50.0	1	433
		1	430
(CH ₂ O) ₃ (Trioxane)	25.0	1	225
		1	221
Et ₂ CO ₃ (Diethyl carbonate)	25.0	1	552
		1	559
EtOCH ₂ CH ₂ OEt (Diethyl Cellosolve)	25.0	1	187
		1	176
		1	140
		1	158

Table V

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TABLE VI

SUMMARY DATA SHEET

[illegible]

Table VI

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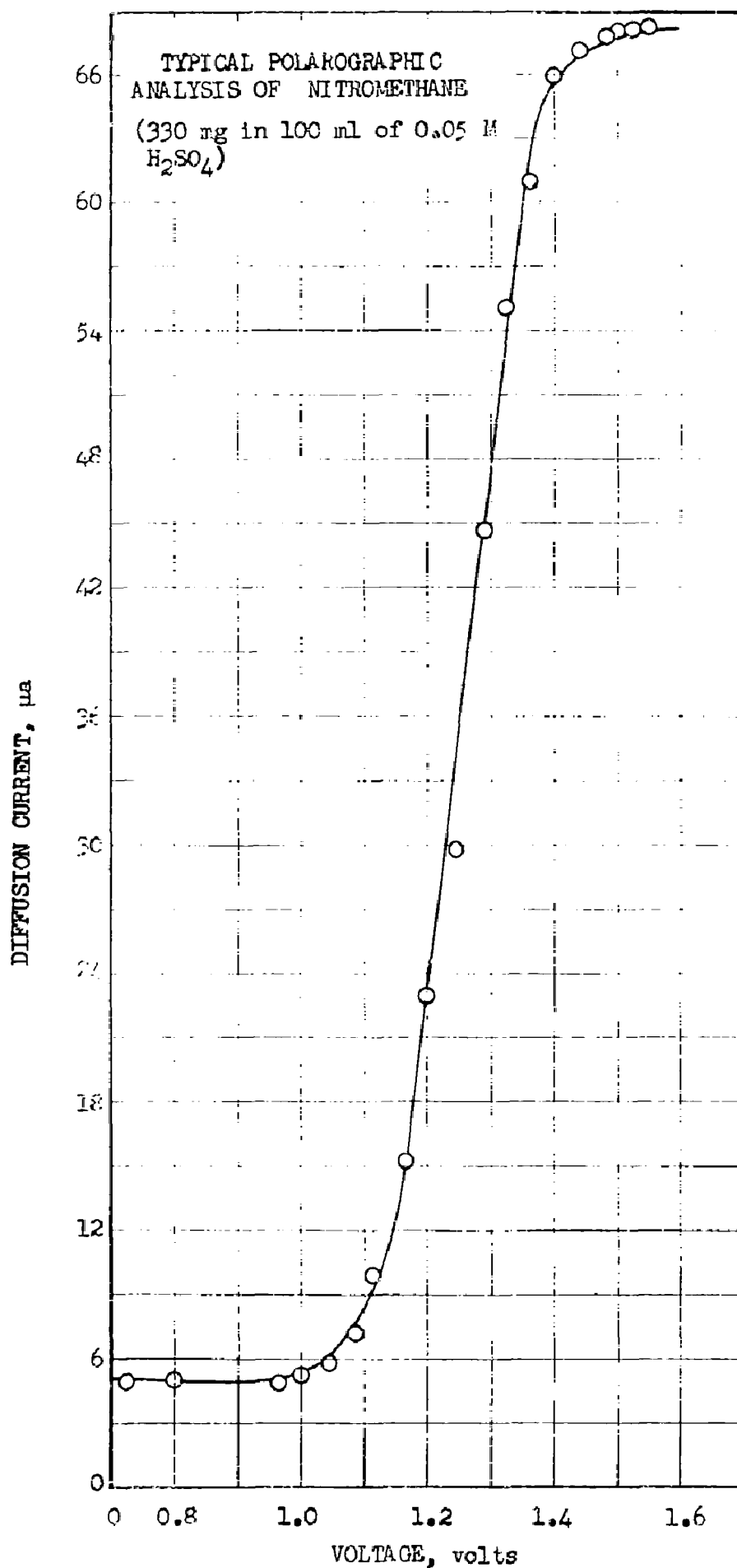


Figure 1

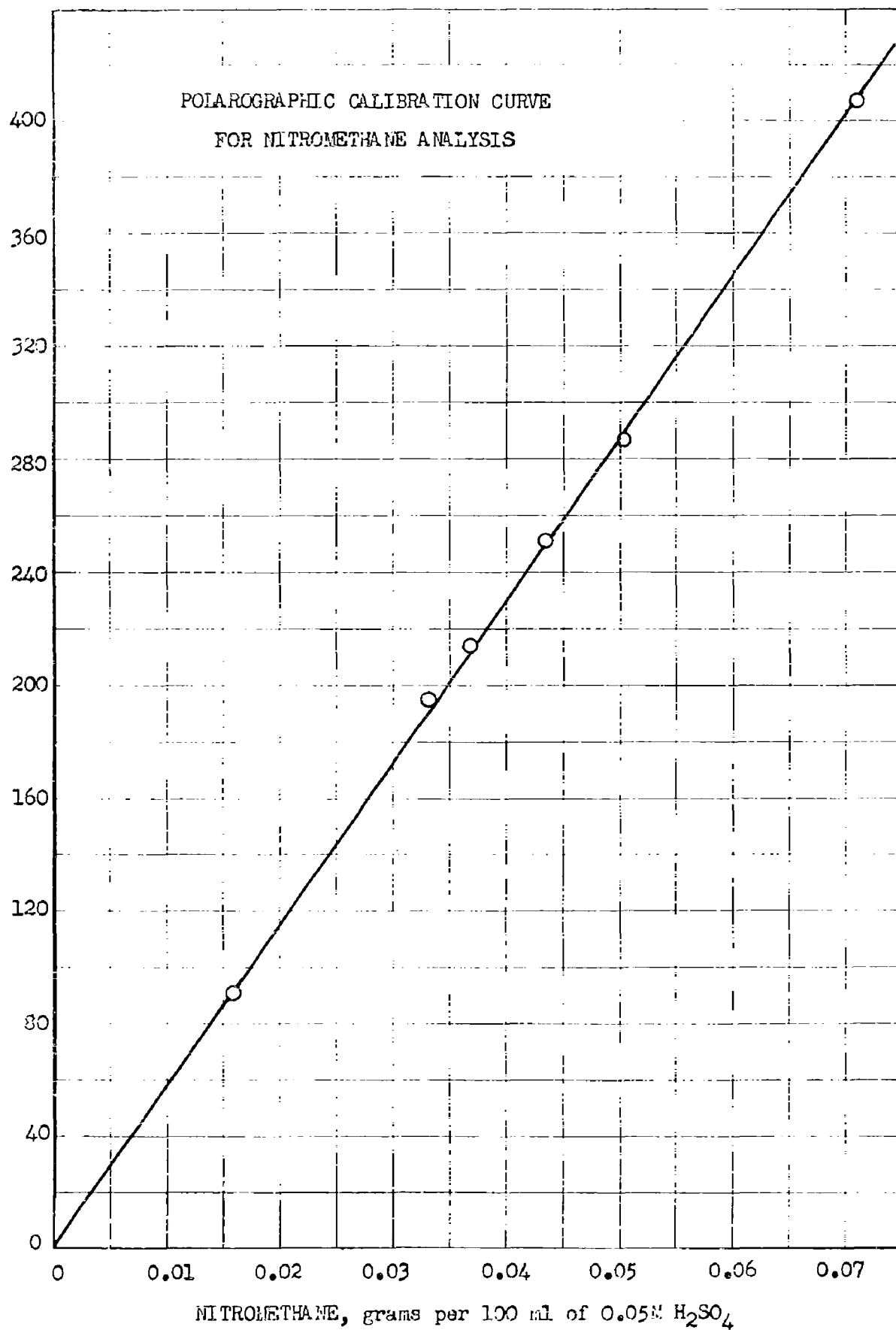
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C-3392 KHM:em 11-25-52

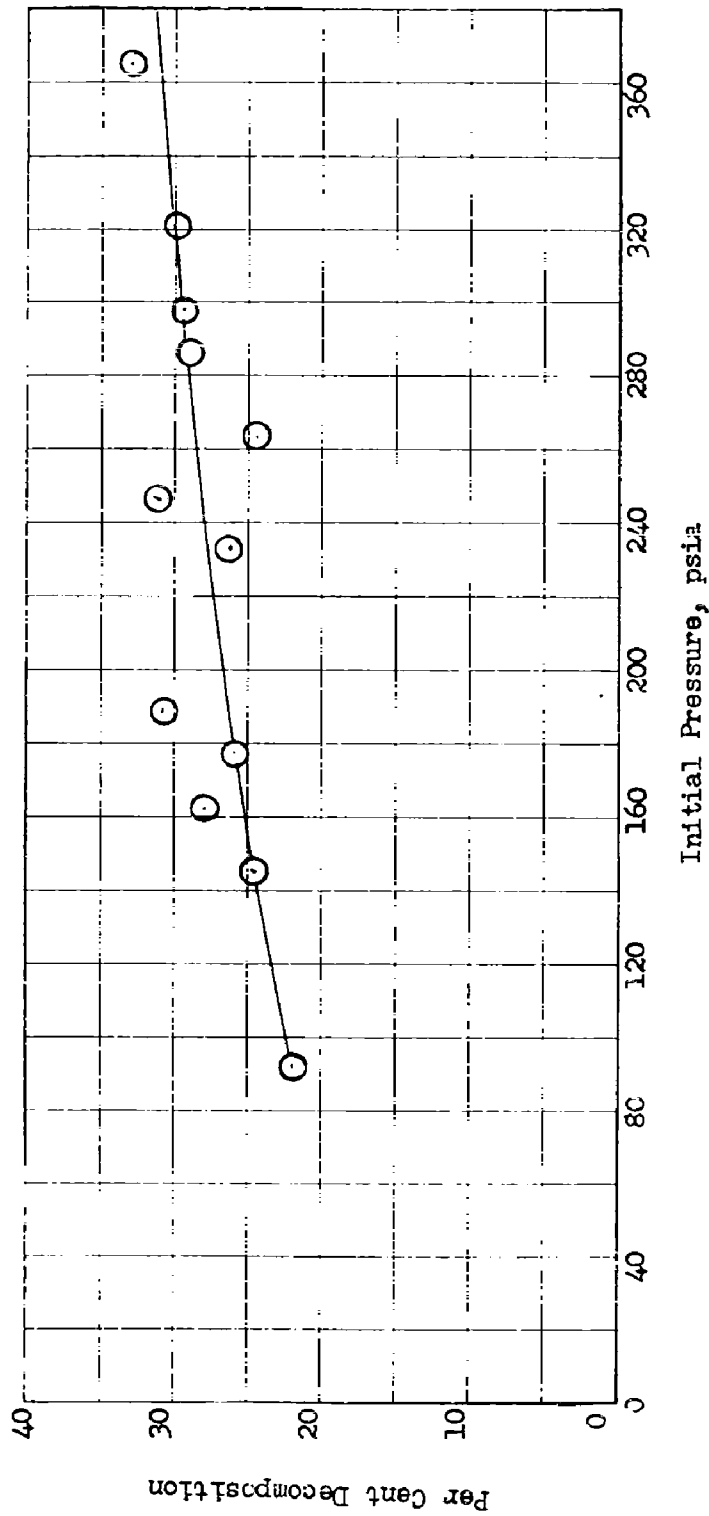
11-26-52

KHM:em

C-3305

DIFFUSION CURRENT, $\mu\text{a} \times 3.77$ $\times 3.77$ 

C-3304 KHM:em 11-26-52

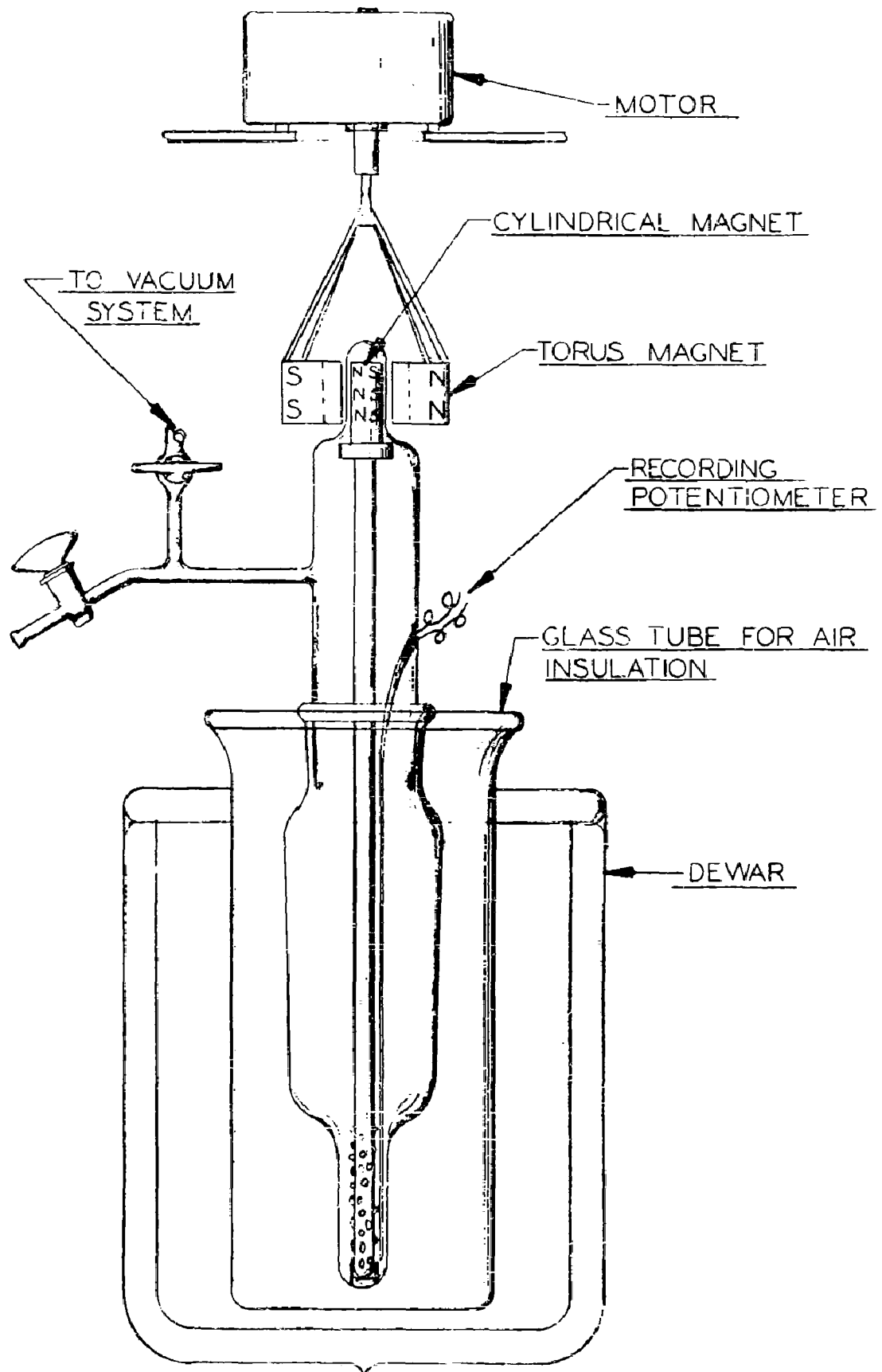


THERMAL DECOMPOSITION OF NITROMETHANE

Temperature = $355 \pm 0.05^\circ\text{C}$

Duration = 31 minutes

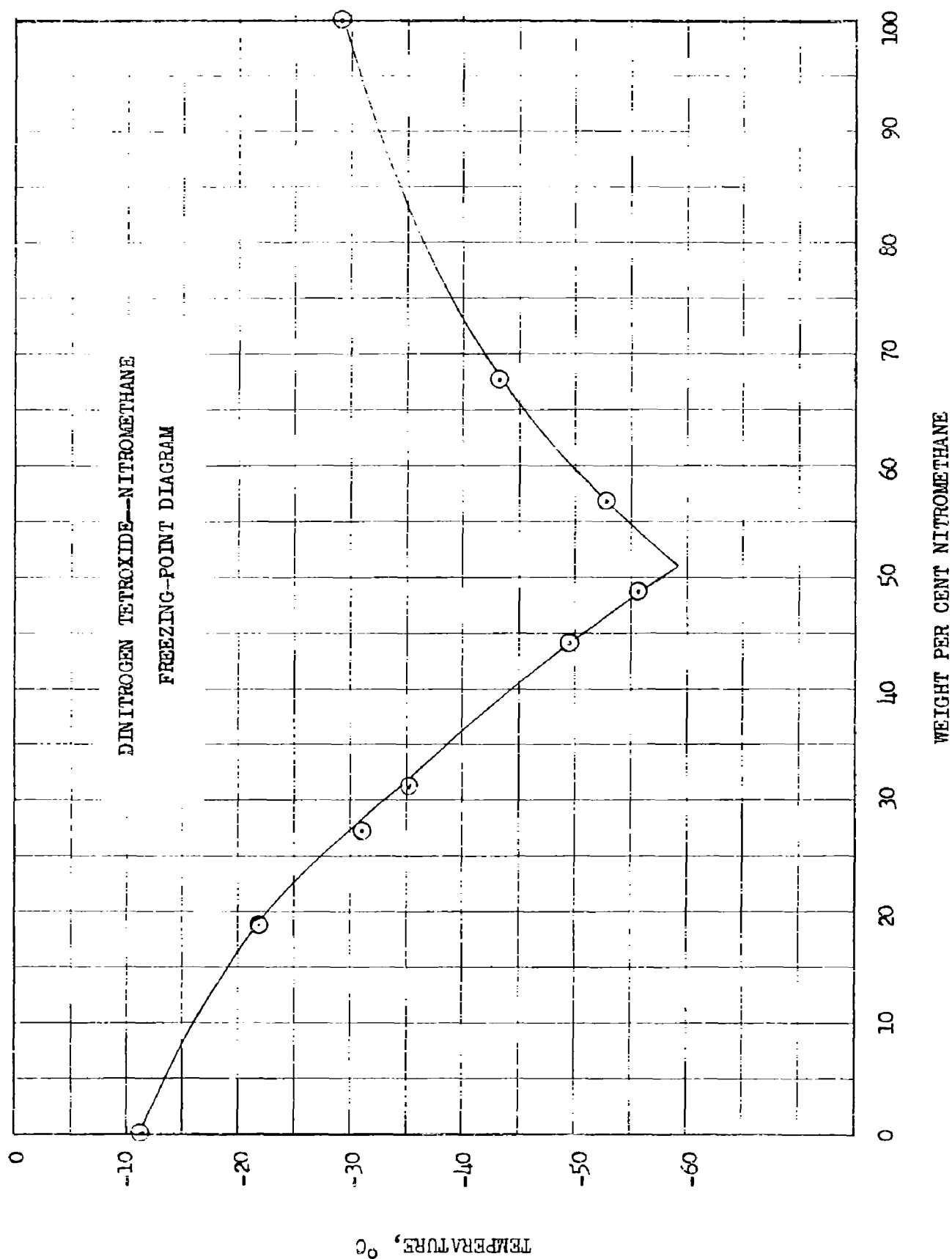
Figure 3

FREEZING - POINT APPARATUS

C-3313

12-6-52 EA E.W.

C-3306 EMW:em 12-4-52



C-3307 EMW:em 12-3-52

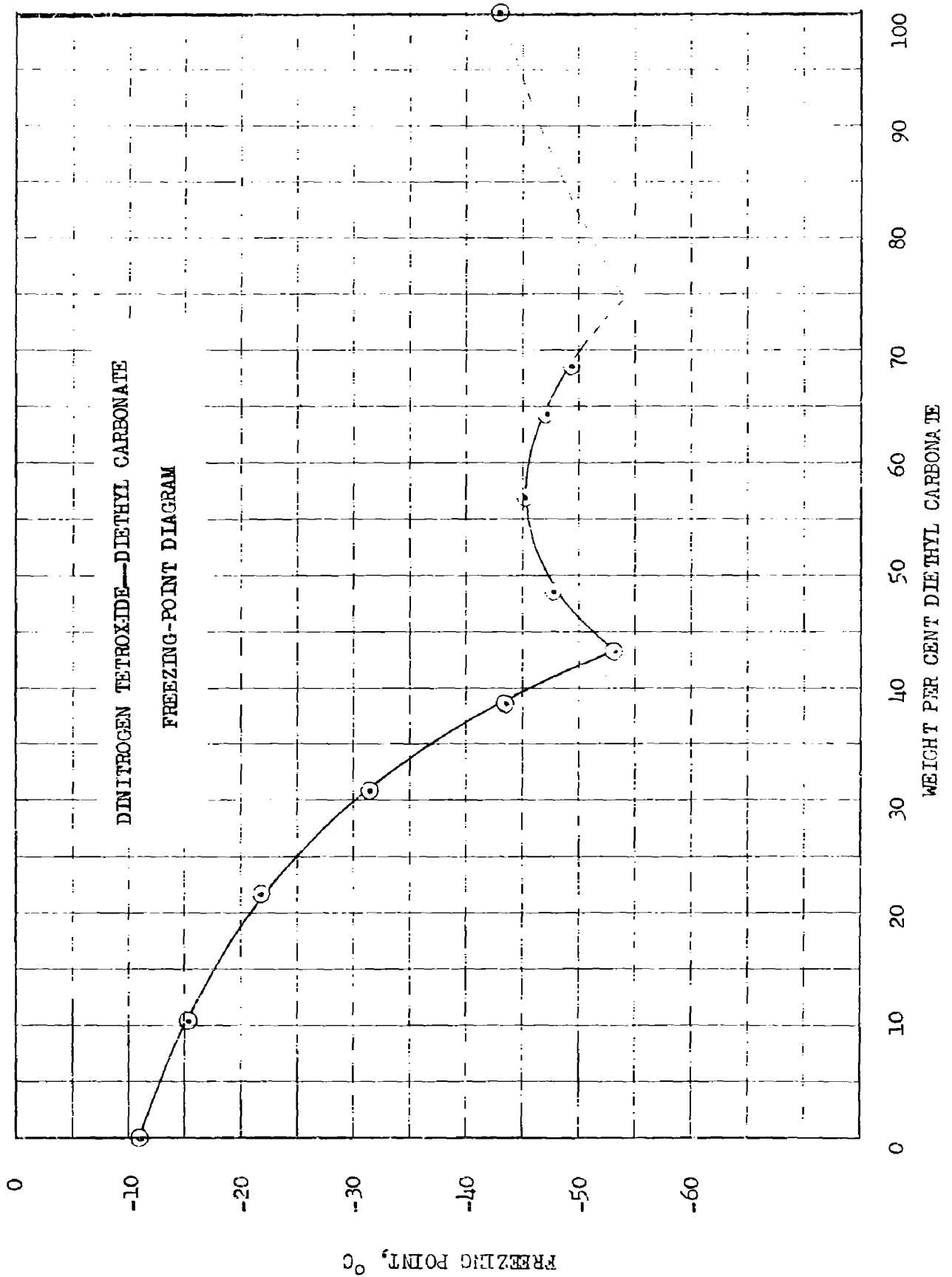


Figure 6

G-3308 EMW:em 12-4-52

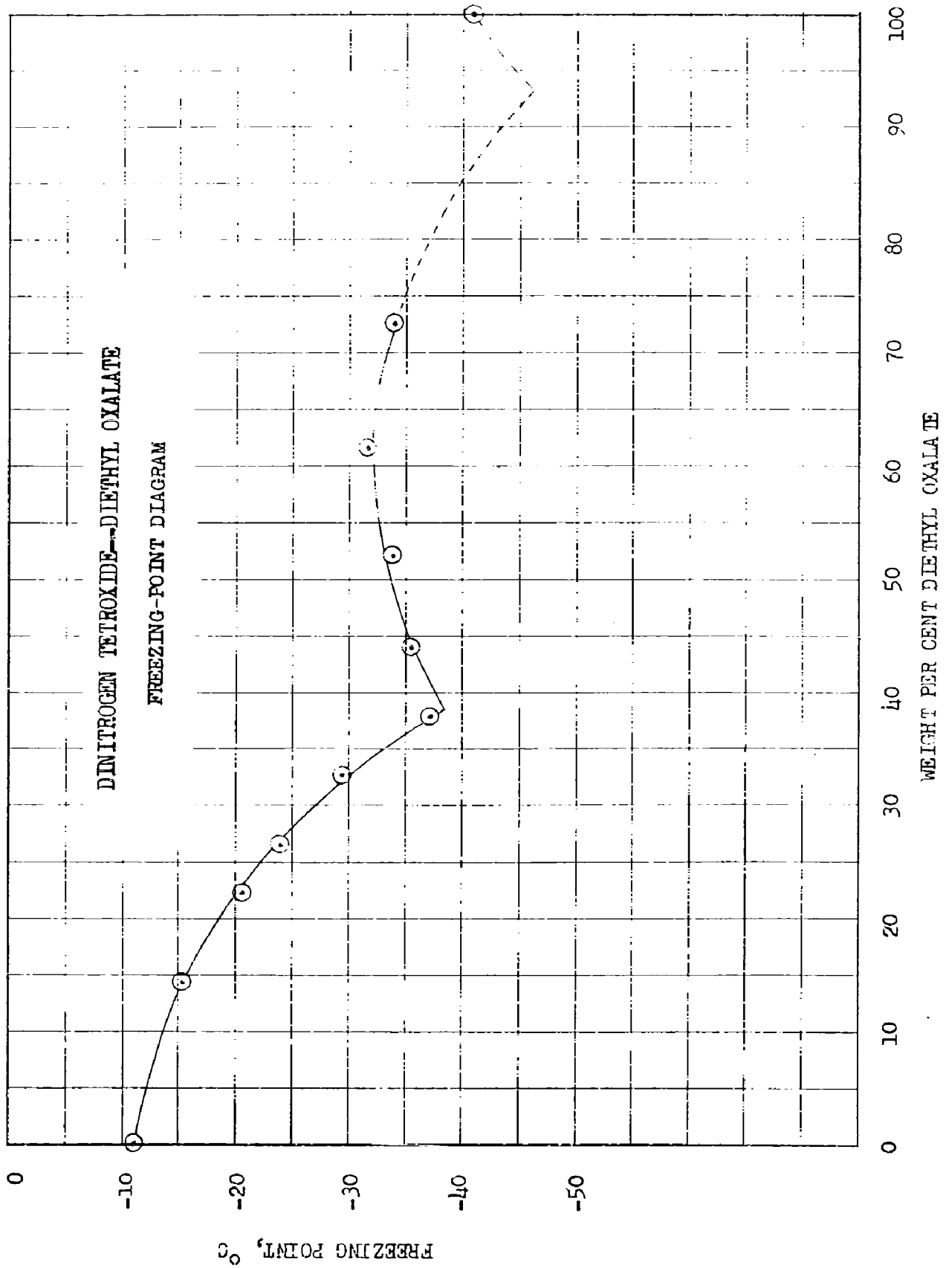
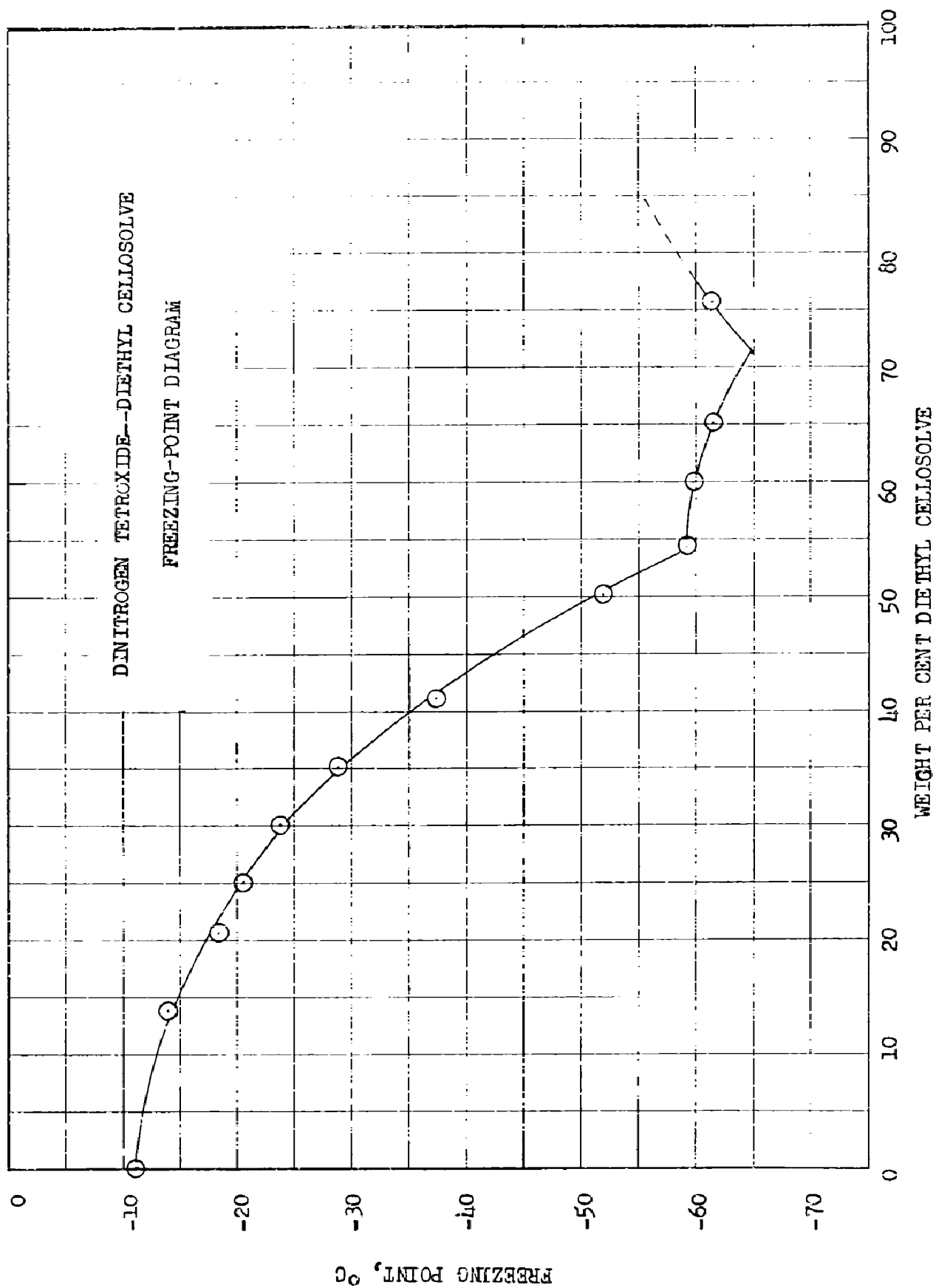


Figure 7

C-3310 EMM:em 12-4-52



C-3312 EMM:em 12-4-52

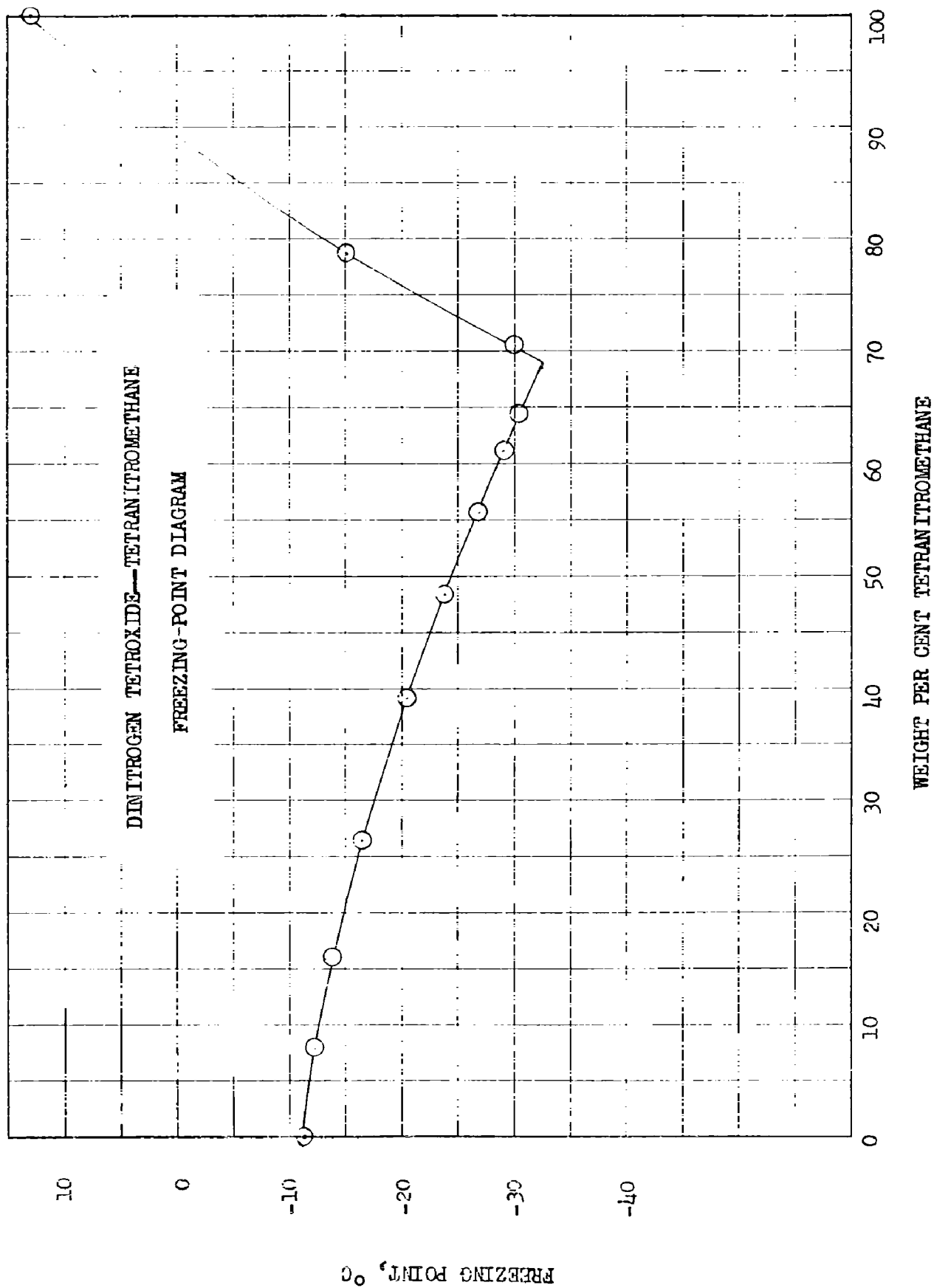
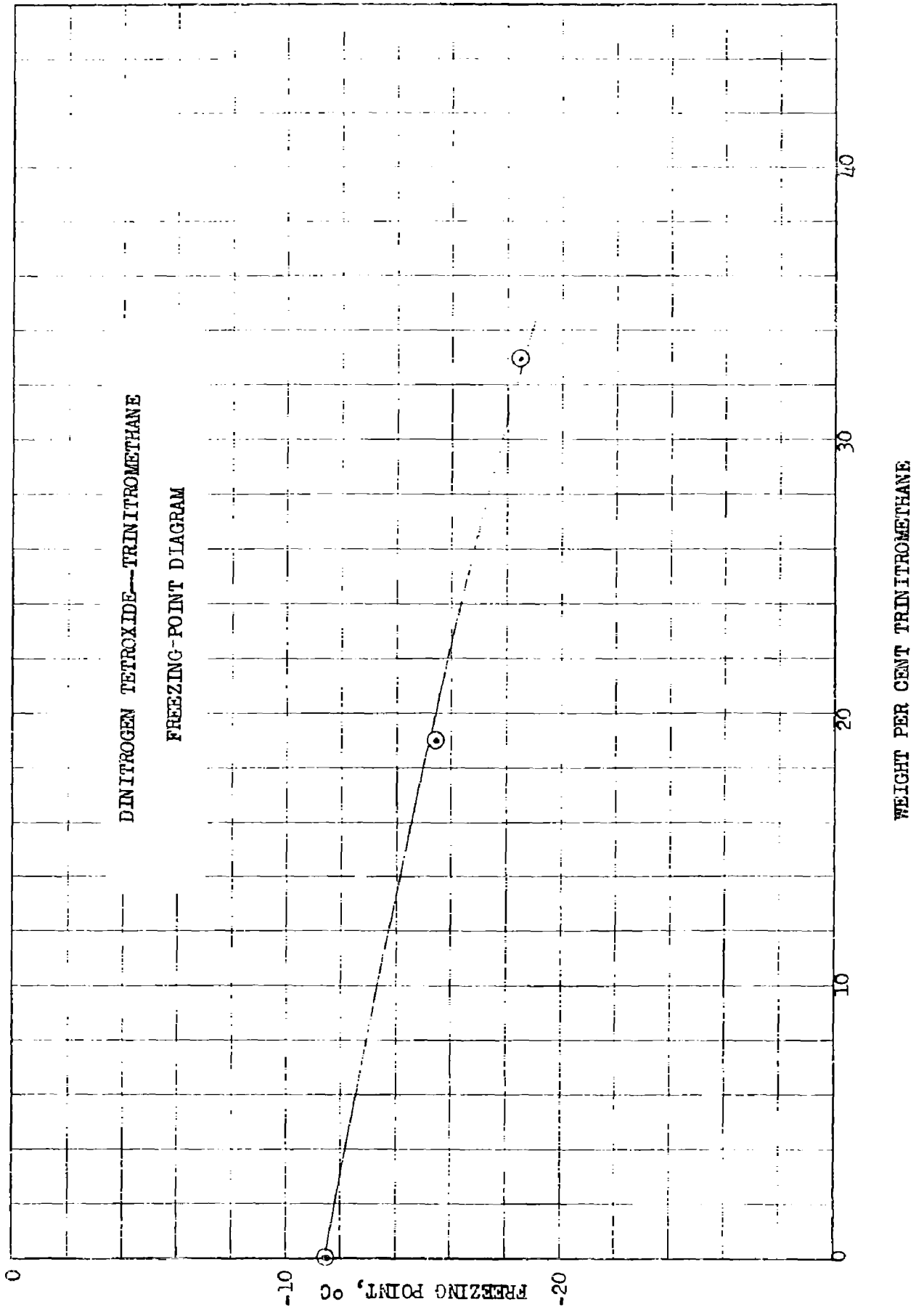
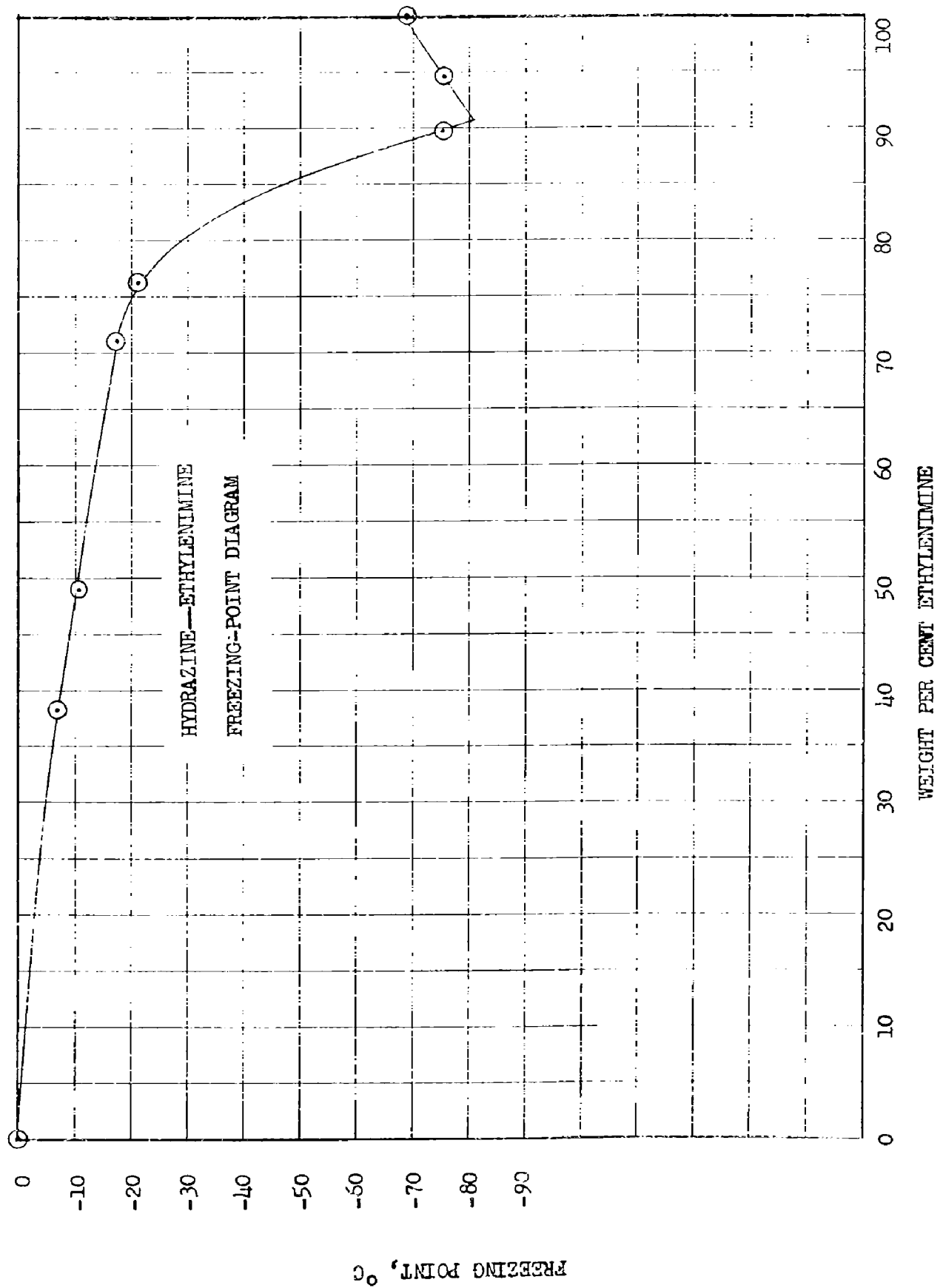


Figure 9

C-3311 EMW:em 12-4-52



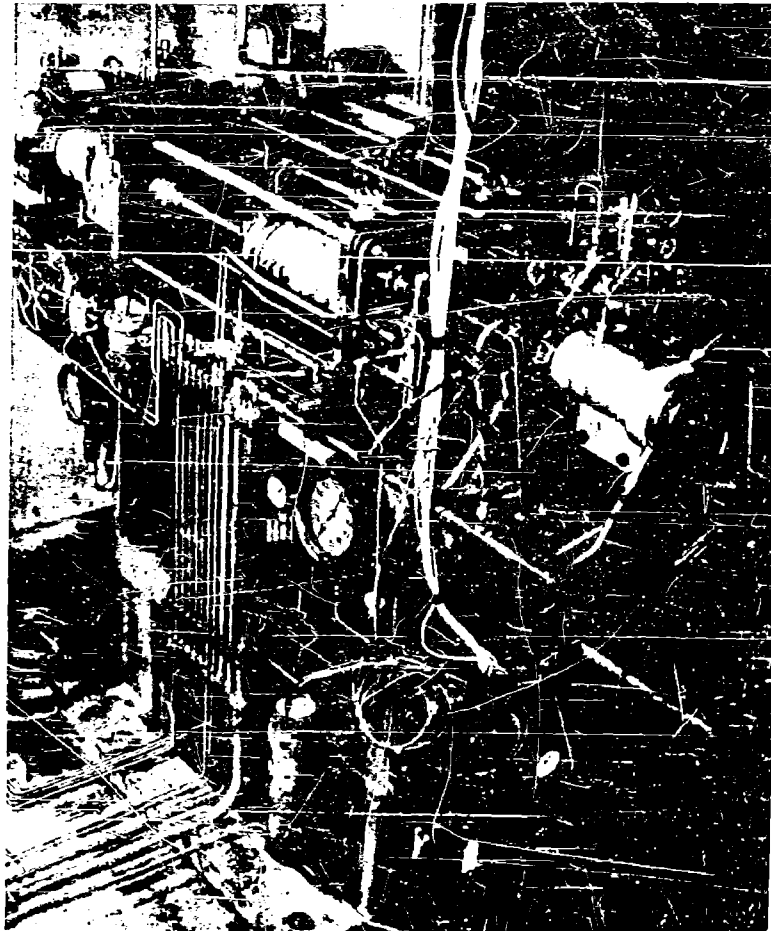
C-3309 EMF:em 12-4-52



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SECURITY INFORMATION



100-lb-Thrust Propellant Tester

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PERFORMANCE VERSUS MIXTURE RATIO
 "HF-D" HYDROCARBON - LIQUID OXYGEN
 Data Corrected For Heat Transfer

Test Nos. D-44-LF 2-6
 Thrust \approx 100 lb
 $P_c \approx$ 300 psia
 $L^* =$ 130 in.

SECURITY INFORMATION

C-3314 EMW 12-9-52

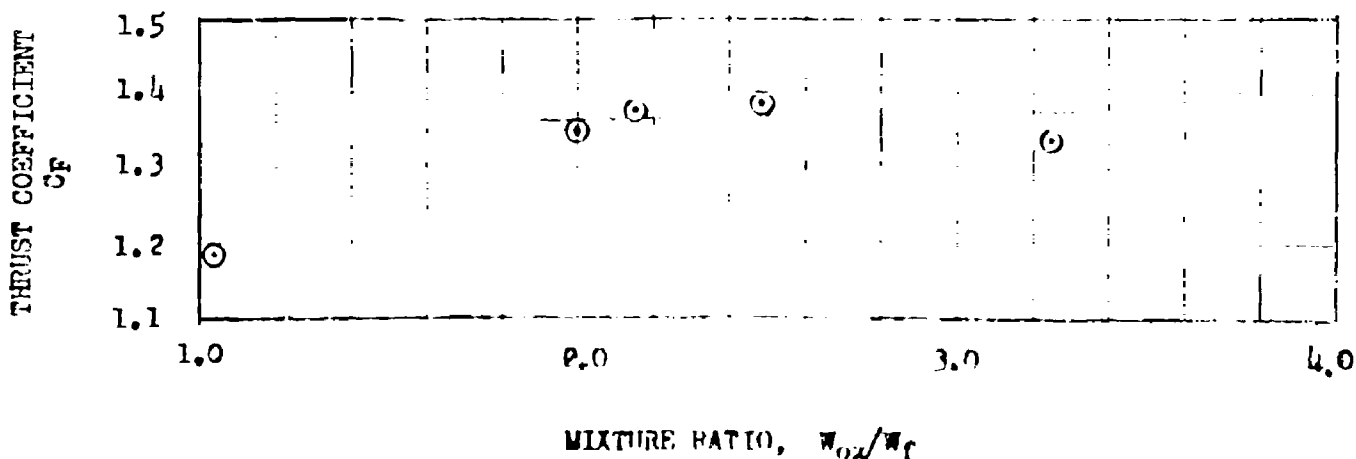
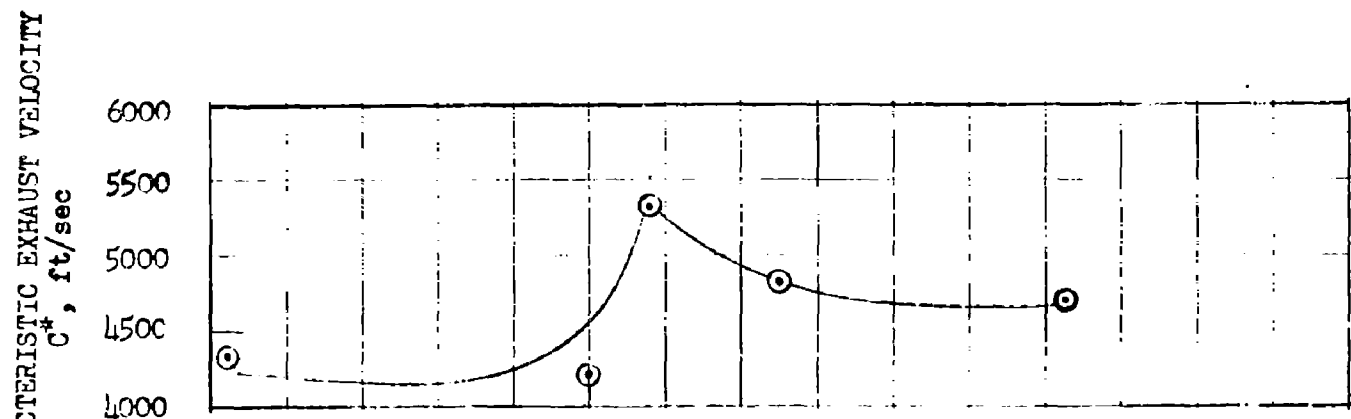
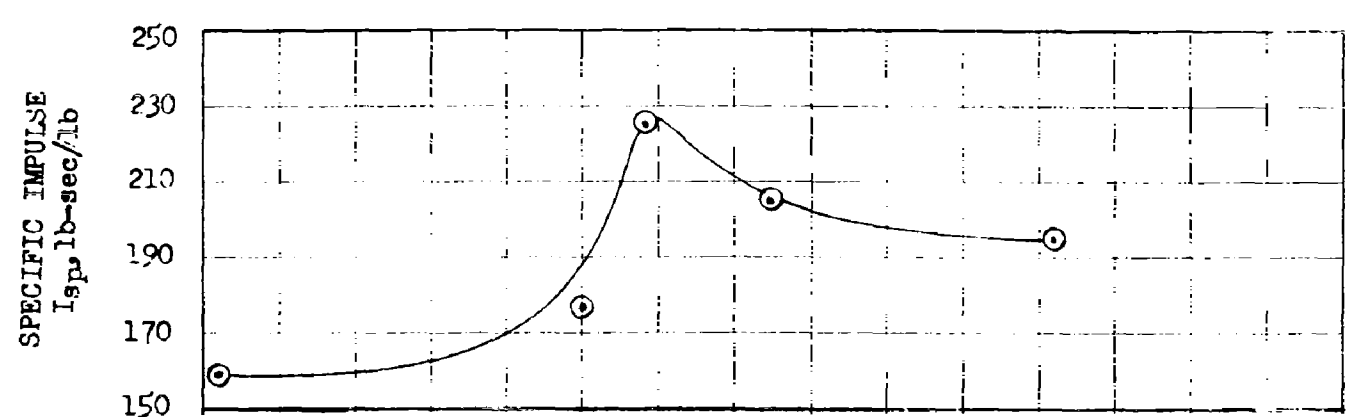


Figure 1j

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SECURITY INFORMATION

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